



Modes of occurrences of scandium in Greek bauxite and bauxite residue

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ABSTRACT

Bauxite and bauxite residue, a by-product of alumina production, were studied using a combination of micro-analytical techniques — electron microprobe wavelength dispersive spectrometry, laser ablation inductively coupled plasma mass spectrometry and μ -Raman spectroscopy. The aim of the work was to reveal the modes of occurrence of scandium (Sc). The motivation behind this effort was to provide mineralogical insight for the support of ongoing development of Sc extraction technologies from bauxite residue. In the analyzed bauxites and residue, Sc is mainly hosted in hematite, where Sc^{3+} probably substitutes Fe^{3+} . The average concentration of Sc in the hematite matrix of bauxite is about 200 mg/kg, while in the bulk sample it ranges from 42 to 53 mg/kg Sc. In bauxite residue, the average concentration of Sc in hematite matrix is about 170 mg/kg, and in the bulk sample it is 98 mg/kg. In bauxite residue, goethite was also identified to host Sc with a concentration of about two times more than in hematite — 330 mg/kg. In bauxite residue, hematite, goethite and zircon host respectively $55 \pm 20\%$, $25 \pm 20\%$ and $10 \pm 5\%$ of the total Sc. The effect of the Bayer process to the modes of occurrences of Sc is minor. The secondary bauxite residue minerals formed during bauxite processing do not capture any or capture very low amounts of Sc. New evidences of Sc leaching behavior from bauxite residue show that Sc is first released from goethite, then from hematite and the unrecovered proportion of Sc is likely associated with zircon.

1. Introduction

Scandium (Sc) has found its way to several advanced applications such as solid oxide fuel cells and Sc-Al alloys because of its unique properties. Despite its use in several applications, the production of Sc remains low, about 10–15 tons per year. It is mainly extracted as a by-product from uranium (U), titanium (Ti), rare earth elements (REE) and apatite production (Gambogi, 2017; Samson and Chassé, 2016). European Commission considers Sc as one of the 26 critical raw materials (European Commission et al., 2017). This means that it has high economic importance while also having high supply risk.

The presence and relative abundance of Sc in bauxites as well as in bauxite residue, a by-product of alumina production, have been acknowledged for decades (Ochsenkühn-Petropulu et al., 1994; Wagh and Pinnock, 1987). However, no large-scale production from these

resources has taken place (Gambogi, 2017). There is a variety of technologies available for the extraction of Sc from bauxite residue and they have been summarized elsewhere (Akçil et al., 2017; Binnemans et al., 2015; Borra et al., 2016; Davris et al., 2017; Liu and Li, 2015; Zhang et al., 2016). It has been estimated that 70% of the world's Sc resources might be found in bauxites (Lavrenchuk et al., 2004). Given that the Bayer process enriches the contents of Sc from bauxite to its residues by a factor of about two, it could be an attractive secondary resource of Sc (Ochsenkühn-Petropulu et al., 1994; Vind et al., 2018). Moreover, an increasing volume of research is attempting to find feasible methods for turning bauxite residue into value-added products, rather than dumping this by-product into disposal areas (Binnemans et al., 2015; Borra et al., 2016; Davris et al., 2017; Evans, 2016). Despite the interest in Sc extraction, very few studies have been conducted to empirically uncover the modes of occurrences of Sc in bauxite residue and studies

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that have targeted this question in bauxite itself are even scarcer (Suss et al., 2017; Zhang et al., 2017, 2016).

The objective of this work is to reveal the modes of occurrences of Sc mainly in bauxite residue as well as in bauxites that represent the parent materials from which the residue is derived from. The primary focus of this paper is therefore on the characterization of Sc in bauxite residue from Aluminium of Greece as well as in Sc-enriched bauxites that they exploit. Explaining the forms in which Sc occurs in bauxite residue minerals will aid the design of Sc extraction technologies from these resources as well as explain, why high recovery rates during Sc extraction are difficult to achieve. A brief literature review is given to provide the state of the art knowledge existing in the field.

2. Geological and geochemical background

Within the geochemical cycle, Sc is known to be present in mafic and ultramafic rocks rather than in felsic rocks. Sedimentary rocks commonly exhibit a very low content of Sc. However, some bauxites and laterites are relatively rich in Sc. Its average concentration in continental crust is 22 mg/kg (Rudnick and Gao, 2003). Sc behaves as a lithophile element and is not affected by the redox conditions of the environment. Sc does not exhibit affinity towards ore forming anions. Because of that, it can be found in small quantities dispersed in many rock forming minerals rather than concentrated in independent mineral phases. Such phases exist (e.g. kolbeckite, thortveitite), but are very rare. Since Sc is scattered in the Earth's crust and deposits with high Sc grade are not formed in natural processes, the production of Sc has relied on resources with Sc content around 100 mg/kg Sc (Das et al., 1971; Samson and Chassé, 2016).

When Sc is present in a bauxite deposit, its distribution is typically associated with REEs, as in south Italian and Sardinian karst bauxite deposits. This distribution pattern is interpreted as a covariance due to the chemical similarities of REEs and Sc rather than as an indication of the formation of any specific Sc-bearing mineral (Blankova et al., 1977; Mongelli et al., 2017). In the Zagrad bauxite deposit (Montenegro), Sc was enriched throughout the bauxite profiles, while some of the lower parts of profiles were particularly enriched in Sc as well as in REEs content (Radusinović et al., 2017).

2.1. Parnassos-Ghiona bauxite deposit

Parnassos-Ghiona bauxite deposit is located in Central Greece, north of the Gulf of Corinth. The bauxite deposit consists of three consecutive horizons as layers, pockets or irregular bodies intercalated in Mesozoic limestones. Because the genesis of the deposit is related to limestones and karst phenomena, it is categorized as a karst bauxite deposit (Bárdossy, 1982; Petrascheck, 1989; Laskou and Economou-Eliopoulos, 2007; Mettos et al., 2008; Valetton et al., 1987). A recent review and a case study of the deposit, with an emphasis on REEs occurrence, is compiled by Deady et al. (2016). The overall average Sc concentration in Greek bauxites is 46 ± 18 mg/kg (sample population $n = 30$) (Laskou and Economou-Eliopoulos, 2007; Laskou, 1991; Ochsenkühn-Petropulu et al., 1994; Laskou and Economou-Eliopoulos, 2013).

3. Bayer process and bauxite residue

The Bayer process is the primary method by which alumina (Al_2O_3) is produced from bauxite ore. In this hydrometallurgical process, caustic soda digestion under elevated temperature and pressure is used to leach soluble alumina minerals from the bauxite ore and subsequently precipitate technically pure aluminum hydroxide. From the pregnant leach solution, the residual mineral matrix is removed as a by-product, commonly termed as bauxite residue or “red mud” (Adamson et al., 2013; Gräfe and Klauber, 2011). The global annual production of bauxite residue is estimated to be about 150 Mt (Evans, 2016). In the process flowsheet of Aluminium of Greece, Metallurgy Business Unit,

Mytilineos S.A., (AoG), about 80% of the bauxite feed is from karst bauxite, mainly Greek origin. About 20% of feed is from lateritic bauxite originating from West Africa (Ghana, Awaso) or Brazil (Porto Trombetas). The method where the hard-to-leach karst (diasporic/boehmitic) bauxite and easily leachable lateritic (gibbsitic) bauxite are used simultaneously in an alumina plant is known as the “sweetening” process. The suspended karst bauxite is digested at a high temperature, and then the lateritic bauxite suspension stream is introduced to the main karst bauxite slurry stream in the appropriate flashing stage. “Sweetening” is utilized to increase the productivity of the plant (Lavalou et al., 1999). The karst bauxite slurry in AoG is digested at about 255 °C (Balomenos et al., 2009) and a pressure of about 5.8–6.0 MPa.

Sc concentrations detected in bauxite residues worldwide range from 41 to 254 mg/kg (Borra et al., 2016; Zhang et al., 2016). Based on various publications that used different analytical techniques, the average concentration of Sc in AoG's bauxite residue is 121 ± 16 mg/kg ($n = 24$) (Alkan et al., 2017; Borra et al., 2015; Davris et al., 2014, 2016; Gamaletsos et al., 2016b; Laskou and Economou-Eliopoulos, 2013; Lymperopoulou et al., 2017; Ochsenkühn-Petropulu et al., 1994; Vind et al., 2017; Yagmurcu et al., 2017). It has been reported that over a 15-year period, the concentration of rare earth elements (REE) as well as Sc in the bauxite residue of AoG has fluctuated only about 8%, indicating to a stable and homogeneous occurrence of Sc in this material (Davris et al., 2017). By 2015, the volume of bauxite residue accumulated in Greece was estimated to be about 5 Mt, resulting from the yearly output of 0.7 Mt (Anagnostou, 2010; Deady et al., 2016). Based on the preceding information, the amount of Sc present in AoG's bauxite residue stocks could be about 600 tons in total.

4. Reports on the modes of occurrences of Sc in bauxite-bauxite residue system

4.1. By indirect methods

Several mineral hosts of Sc have been suggested for bauxite and its residue system. A correlation between Sc and P_2O_5 occurrence has been reported at least in three cases. Phosphate phases, like variscite, have been considered as Sc host minerals (Radusinović et al., 2017; Suss et al., 2017; Wagh and Pinnock, 1987).

Derevyankin et al. deduced from their analysis of Sc behavior in the Bayer process that Sc is most likely bound with iron oxides and titanium dioxides in bauxite (Derevyankin et al., 1981). Correlations between Ti and Sc behavior during leaching tests and the assumed mineralogical association of these metals have been reported at least three times for the case of AoG's bauxite residue (Bonomi et al., 2017b; Ochsenkühn-Petropulu et al., 1994; Rivera et al., 2017).

Mongelli et al. suggested on the basis of established association of Sc^{3+} with Fe^{3+} and geochemical data of several Italian bauxite deposits that Sc might occur in detrital iron minerals like titanomagnetite (Mongelli et al., 2017). It was hypothesized that Sc might be bound to iron oxides of bauxite residue, either by substituting Fe^{3+} or by its adsorption on iron oxides mineral surfaces, by analyzing the behavior of Sc during leaching experiments (Borra et al., 2015).

4.2. By direct methods

As the result of direct investigation by electron microprobe, the first reports referring to Sc occurrence in certain bauxite minerals date back to 1973 and indicate its presence in detrital zircon (Bárdossy and Pantó, 1973). It is a well-established fact that Sc can be found in zircon, as reported in several bauxite deposits: Mazaugues (France), Campo Felice (Italy), bauxites of Southern Apennines (Italy) (Bárdossy and Pantó, 1973; Boni et al., 2013; Mongelli et al., 2017; Radusinović et al., 2017). In Schugorsk deposit (Urals, Russia), zircon grains exhibited altered rims that contained up to 3.5 wt% Sc (Mordberg et al., 2001). The

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